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GC-MS and GC-FID Analysis of Citronella Oil Products for Indicator Ingredient Identification

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Abstract : Citronella oil, an essential oil extracted through steam distillation from the leaves and stems of *Cymbopogon*, is a natural complex substance (NCS) regulated by the Korean government for its use in insect repellents. The component ratios of NCSs like citronella oil vary due to differences in manufacturing processes and origins, presenting a challenge in identifying and quantifying these substances in consumer chemical products. This study analysed ten commercially available products of the most commonly used types of citronella oil, specifically Java and Ceylon types, using gas chromatography (GC)-mass spectrometry (MS) and GC with flame ionization detection (FID). Through chromatographic data, we aimed to determine the components that can qualitatively identify citronella oil and the indicator ingredients that can be used for content analysis.

Key words : citronella oil, flame ionization detection, gas chromatography, mass spectrometry

Introduction

Citronella oil is an essential oil obtained by steam distillation of the fresh or dried aerial parts of *Cymbopogon* grasses and has been widely used in insect repellents.[1,2] There are two commercillay available types of citronella oil, Java type, derived from *Cymbopogon winterianus*, and Ceylon(Sri Lanka) type derived from *Cymbopogon nardus*.[1,2]

The international organization for standardization (ISO) has established specifications for certain characteristics of both types of citronella oils (ISO 3848[3] for Java type and ISO 3849[4] for Ceylon type), aiding in the assessment of their quality.[5,6] These specifications include the content ranges of the major ingredients in each type of citronella oil. These ranges were calculated using the area normalization method, based on chromatographic profiles obtained through gas chromatography-flame ionization detection (GC-FID).

Citronella oil is also listed as an allowed main ingredient in insecticides and repellents according to the Korean Ministry of Environment's notice (Notice No. 2023-163), 'Designation of, and safety and labeling standards for, consumer chemical products subject to safety verification'. Therefore, it is necessary to determine its content in consumer chemical products containing citronella oil. According to the Korean Ministry of Environment's notice (Notice No. 2022-26), 'Regulations on testing and inspection standards and methods for consumer chemical products subject to safety verification', the content of citronella oil (Java type, CAS No. 8000-29-1) in a product is determined by gas chromatography-mass spectrometry (GC-MS) as the sum of the concentrations of its major constituents, citronellol and geraniol.

However, essential oils including citronella oil are a type of natural complex substances (NCS), derived from plant origins and obtained through purification processes and the chemical composition of these NCSs can vary depending on the processing method, including extraction and distillation, the growth location of the plant, and the specific parts of the plant utilized.[7] Therefore, these oils are categorized as substances of unknown or variable composition, complex reaction products, or biological materials (UVCBs).[8,9] Consequently, quantifying and identifying substances with variable compositions based on some of their ingredients can be challenging and should be performed with caution.

In this study, 10 commercially available citronella oil

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products were analyzed by GC-FID and GC-MS, and the results were used to determine appropriate indicator ingredients of citronella oil that can be used to identify citronella oil in products or determine its content.

Experimental

Materials and chemicals

Five Java type and five Ceylon type citronella oil products from various countries of origin were selected and purchased from online stores. Details for purchased oil products are listed in Table 1. High purity helium (He, 99.999%), nitrogen (N_2), air gases were purchased from Good Gas Co. (Pocheon, Korea). Ethyl acetate (EA, 99.9% purity for HPLC, GC, and residue analysis) was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA).

GC-MS and GC-FID analysis

For GC analysis, a citronella oil sample was diluted to 1000 ppm or lower with EA and analyzed. GC-MS analysis was performed using a GC-2010 Plus gas chromatograph with an AOC-20 autosampler (Shimadzu, Kyoto, Japan), coupled to a quadrupole mass spectrometer (GCMS-QP2020, Shimadzu). For GC-FID analysis, a Nexis GC-2030 gas chromatograph, equipped with a FID and an AOC-20is autosampler (Shimadzu) was utilized.

GC separation was conducted using a nonpolar DB-5MS column (30 m × 0.25 mm ID, 0.25 μm film thicknes, Agilent Technologies, Santa Clara, CA, USA) for GC-MS analysis or a nonpolar SH-5 column (30 m × 0.25 mm ID, 0.25 μm film thicknes, Shimadzu) for GC-FID analysis. Both columns have the same stationary phase composition (5% diphenyl/95% dimnethyl polysiloxane). He gas was used as a carrier gas, with a flow rate of 1.5 mL/min. One microlitere of a sample injected in split mode (25:1) and injection temperature was set to 280°C. The column oven temperature was maintained at 50°C for 1 min before being raised to 100°C at a rate of 10°C/min. Then, the temperature was increased to 220°C at a rate of 20°C/min and held for 5 min. Lastly, the temperature was raised to 300°C at a rate of 10°C/min and held for 1 min.

For MS analysis, electron impact ionization (70 eV) was employed and spectra was collected through *m/z* 30–500. Ion source temperature and interface temperature were set to 230°C and 260°C, respectively. For FID analysis, He makeup gas was used at a flow rate of 24.0 mL/min, Flow rates for H_2 and air were set to 32.0 mL/min and 200.0 mL/min, respectively and detector temperature was 300°C.

Data processing including peak identification and peak area integration was performed using a GCMS solution software (Shimadzu) for GC-MS data and a GC solution software (Shimadzu) for GC-FID data.

Table 1. Citronella oil sample information.

Type	Sample ID	Origin	Parts used
Java	J1	China	Not listed
	J2	Nepal	Leaves and stems
	J3	Spain	Not listed
	J4	India	Leaves and stems
	J5	Indonesia	Leaves
Ceylon	C1	Sri Lanka	Leaves
	C2	India	Grass
	C3	Indonesia	Leaves
	C4	England	Dry grass
	C5	Australia	Leaves

Results and Discussion

GC-MS analysis of citronella oil products

Ten citronella oil products underwent GC-MS analysis, and the compounds corresponding to the resulting peaks were identified by matching the obtained EI mass spectra with those deposited in the national institute of standards and technology (NIST) mass spectral library (NIST 17, Gaithersburg, MD, USA). Results are summarized in Tables 2, 3, and 4. Five replicates of each sample were analyzed and retention time (RT) of each compound was found to be consistent with standard deviation of 0.002 min or less.

For the Java type samples, the total number of compounds identified did not vary significantly, remaining between 25 and 30 (Table 2) and the 14 main ingredients listed in ISO 3848 were identified in all samples (Table 3). In contrast, the Ceylon type samples exhibited a relatively large variation in the total number of compounds identified, ranging from 25 to 42. All seven compounds listed in ISO 3849 were detected only in one sample (C1) whose origin is Sri Lanka, while only 3 to 5 out of these seven compounds were detected in the remaining samples (Tables 2 and 4).

Table 2. GC-MS results obtained from citronella oil samples.

Type	Sample ID	Total identified compounds	Detection frequency of ISO listed compounds
Java	J1	27	14/14
	J2	30	14/14
	J3	29	14/14
	J4	29	14/14
	J5	25	14/14
Ceylon	C1	42	7/7
	C2	26	3/7
	C3	27	5/7
	C4	25	4/7
	C5	27	4/7

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Table 3. GC-MS and GC-FID analysis results for citronella oil, Java type products.

No.	RT (min) in GC-MS[a]	Chemical Name	DF[b]	ISO listed % area (FID)[c]		GC-FID analysis results of Sample J1~J5						
				Min. %	Max. %	% area[d] J1	J2	J3	J4	J5	Average[e]	RSD (%)[f]
1	6.44	Limonene	5/5	2.0	5.0	3.80	3.41	3.82	3.50	3.96	3.70	6.3
2	7.84	Linalool	5/5	0.5	1.5	0.96	0.75	0.78	0.88	0.91	0.86	10.2
3	9.31	Citronellal	5/5	31.0	40.0	34.65	37.99	36.92	31.92	34.76	35.25	6.7
4	9.59	Isopulegol	5/5	0.5	1.7	0.54	0.53	0.48	0.61	0.47	0.53	10.6
5	11.34	Citronellol	5/5	8.5	14.0	12.72	11.77	11.40	13.05	13.28	12.44	6.6
6	11.77	Geraniol	5/5	20.0	25.0	22.57	23.29	25.00	22.52	21.92	23.06	5.2
7	12.07	Geranial	5/5	0.3	1.0	0.52	0.82	0.81	0.60	0.43	0.64	27.8
8	13.13	Citronellyl acetate	5/5	2.0	4.0	2.51	2.11	2.16	2.67	2.53	2.40	10.3
9	13.18	Eugenol	5/5	0.5	1.0	1.03	0.82	0.83	0.85	1.07	0.92	12.9
10	13.45	Geranyl acetate	5/5	2.5	5.5	3.07	3.23	3.37	3.30	2.73	3.14	8.2
11	13.61	β-Elemene	5/5	0.7	2.5	3.13	1.74	1.68	3.42	3.03	2.60	31.7
12	14.49	Germacrene-D	5/5	1.5	3.0	1.82	1.02	1.39	1.45	2.13	1.56	27.4
13	14.76	δ-Cadinene	5/5	1.5	2.5	2.47	1.43	1.50	2.24	2.50	2.03	25.8
14	14.99	Elemol	5/5	1.3	4.8	3.45	3.04	2.83	4.49	3.47	3.46	18.6

[a]Average retention time (RT) obtained from 5 analyses of J1
[b]Detection frequency (DF) out of 5 Java type samples
[c]Minimum and maximum percent area values listed in ISO 3848
[d]Average percent area value obtained from five replicate measurements of each sample
[e]Average of percent area values of five different Java type samples (J1–J5)
[f]Relative standard deviation (RSD) of percent area values of five different Java type samples (J1–J5)

Table 4. GC-MS and GC-FID analysis results for citronella oil, Ceylon type products.

No.	RT (min) in GC-MS[a]	Chemical Name	DF[b]	ISO listed % area (FID)[c]		GC-FID analysis results of Sample C1~C5						
				Min. %	Max. %	% area[d] C1	C2	C3	C4	C5	Average[e]	RSD (%)[f]
1	5.19	Camphene	1/5	7.0	10.0	9.29	n.d.[g]	n.d.	n.d.	n.d.	9.29	-
2	6.44	Limonene	4/5	7.0	11.5	8.28	n.d.	3.26	3.28	3.29	4.53	55.2
3	9.31	Citronellal	5/5	3.0	6.0	2.20	25.39	37.86	40.74	40.58	29.36	56.0
4	10.06	Borneol	1/5	4.0	7.0	7.48	n.d.	n.d.	n.d.	n.d.	7.48	-
5	11.34	Citronellol	5/5	3.0	8.5	4.41	14.21	10.20	9.53	9.56	9.58	36.4
6	11.77	Geraniol	5/5	15.0	23.0	20.88	28.45	22.32	22.43	22.48	23.31	12.6
7	14.51	Methyl isoeugenol	2/5	7.0	11.0	4.81	n.d.	1.12	n.d.	n.d.	2.96	-

[a]Average retention time (RT) obtained from 5 analyses of C1
[b]Detection frequency (DF) out of 5 Ceylon type samples
[c]Minimum and maximum percent area values listed in ISO 3849
[d]Average percent area value obtained from five replicate measurements of each sample
[e]Average of percent area values of five different Java type samples (C1–C5)
[f]Relative standard deviation (RSD) of percent area values of five different Java type samples (C1–C5)
[g]n.d.: not detected

Compounds detected in all Ceylon type samples were citronellal, citronellol, and geraniol.

These results can be easily confirmed visually with representative GC-MS chromatograms (Figure 1). It was hard to distinguish one Java sample from the other based on chromatographic profiles (Figure 1 (a) and (b)), whereas chromatographic profiles of Ceylon type samples were clearly distinguished from each other (Figure 1 (c) and (d)).

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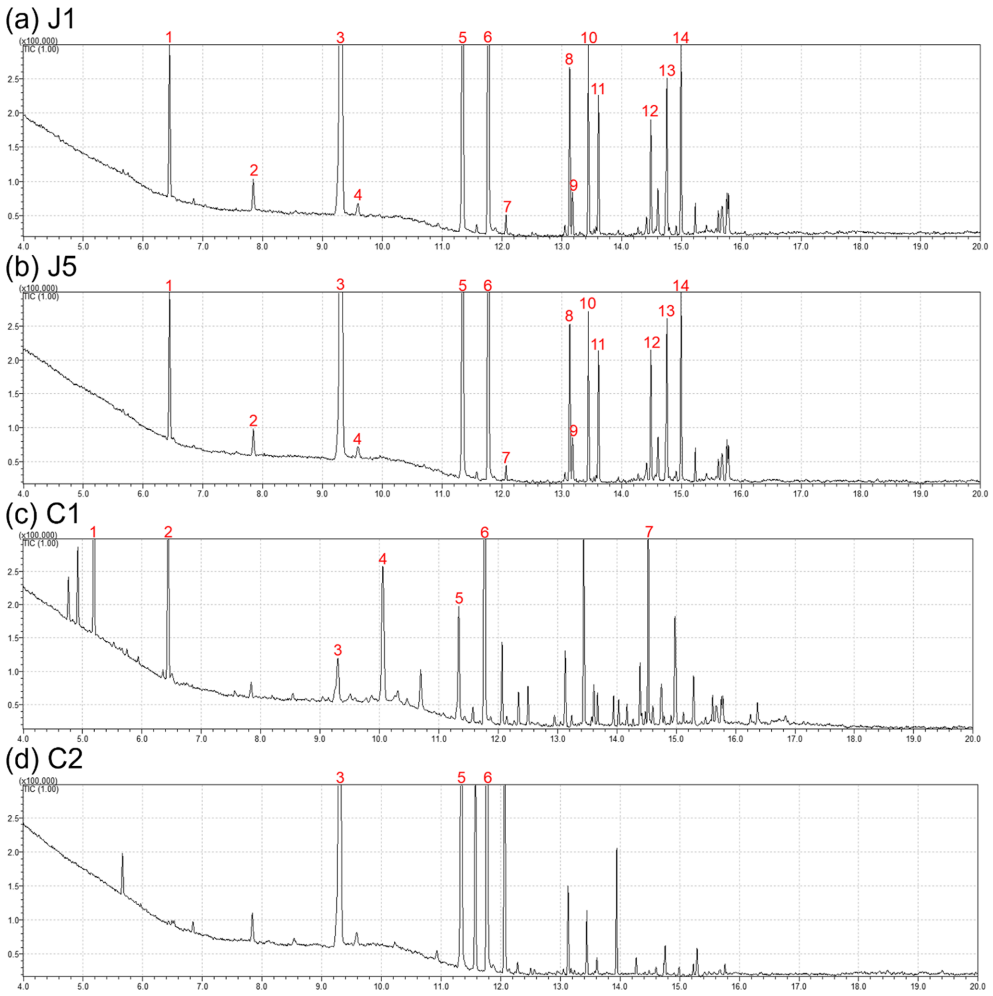

Figure 1. Representative GC-MS chromatograms of Citronella oil products, (a) J1, (b) J5, (c) C1, and (d) C2. The numbers on the peaks in chromatograms (a) and (b) correspond to the compound numbers listed in Table 3, whereas the numbers on the peaks in chromatograms (c) and (d) correspond to the compound numbers listed in Table 4.

GC-FID analysis of citronella oil products

Ten citronella oil products were also analyzed by GC-FID with the same separation condition with GC-MS analysis. Based on obtained chromatographic profiles, percent areas of the peaks annotated as the ISO listed compounds were calculated by the area normalization method. The average percenct area values of the ISO listed compounds obtained from 5 replicate measurements are listed in Tables 3 and 4. Percent area of each compound was consistent through replicate measurements with the relative standard error (RSE) of 2.5% or less.

For the Java type samples, all the obtained percent area values for all ISO compounds except β-elemene in the samples J1, J4, and J5 are within the ranges listed in ISO 3848 (Table 3). Given the UVCB nature of essential oils, such consistency in component content is uncommon, yet it represents a significant positive outcome for ensuring reliable content analysis.

However, there was no consistency in percent area values in the Ceylon type samples, as expected from the GC-MS results (Table 4). Even three compounds (citronellal, citronellol, and geraniol) detected in all Ceylon samples varied significantly in their percent area values. Although a small number of Ceylon samples were analyzed in this study, it can be expected that determining the content of the Ceylon type citronella oil in a given consumer chemical product through the concentration of its constituents would be unreliable. Therefore, we decided to consider only Java type for the selection of indicator ingredients for content analysis and identification.

Selection of indicator ingredients for Java type

Based on the GC-MS and GC-FID analysis results for the Java type samples, we sought to determine indicator ingredients that could be utilized to determine the content of citronella oil in consumer chemical products. Our criteria for selecting indicator ingredients were as follows: first, ingredients with top 5 in its percent area value; second, a relative standard devi-

ation (RSD) of percent area values between samples of less than 10%; and third, whether the compounds were specific to citronella oil. Based on the results in Table 3, there are four ingredients (citronellal, geraniol, citronellol, and limonene) that satisfy the first and second conditions.

Among these 4 ingredients, limonene was excluded first because it is a prevalent terpene compound found in nature and is a major ingredient of the essential oils of citrus fruits such as lemons, oranges, and limes[10-12] and thus it does not satisfy the third criterion.

Chemical structures of indicator ingredient candidates, citronellal, geraniol, and citronellol, for citronella oil content analysis are shown in Figure 2. Citronellal, a terpene, is the predominant component of citronella oil, characterized by its central nervous system depressant, hypnotic, and antioxidant attributes.[13-15] Geraniol, an acyclic monoterpene allyl alcohol, emits a rose-like aroma and is renowned for its properties as a repellent, insecticide, and in antitumor applications.[16,17] Citronellol, differing from geraniol by the presence of a single double bond (as illustrated in Figure 2), is notable for its antibacterial, antifungal, antispasmodic, and anticonvulsant activities.[16,18]

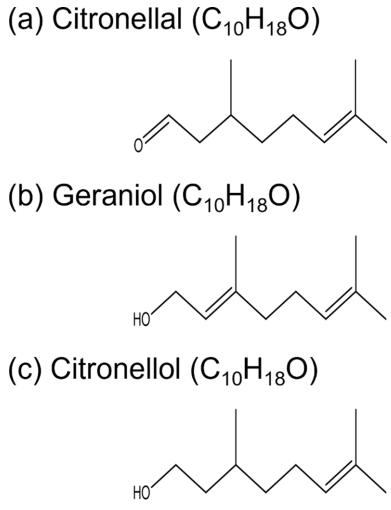

Figure 2. Indicator ingredient candidates for citronella oil, (a) citronellol, (b) geraniol, and (c) citronellol.

To estimate quantitative performance of these indicator ingredient candidates as well as to determine components which can be utilized for identifying Java type citronella oil, a citronella oil J1 samples with various concentrations ranging from 2 to 1000 ppm were analyzed using GC-MS. All 14 compounds listed in ISO 3848 were detected in samples of 100 ppm or higher. Given the 1-10 wt% citronella oil content in a typical insect repellent (spray type) and the 10-100 fold dilution of the product during sample preparation for GC-MS analysis, all 14 ISO listed compounds can be utilized for identifying Java type citronella oil. We recommend identifying as many of the 14 ISO-listed compounds as possible to determine the presence of Java type citronella oil in a given product, and suggest that at least 10 ISO-listed compounds whose percent area value of 1% or greater be identified.

Three indicator ingredient candidates for content analysis were detected with a signal-to-noise ratio of 10 or higher, even when the sample was diluted down to 5 ppm. Table 5 lists the characteristics of calibration curves constructed using individual or combinations of indicator ingredient candidates. The effectiveness of a calibration was evaluated based on the coefficient of determination (R^2) and the RSD of the calibration factor (CF), a measure of the chromatographic response of a target analyte relative to the mass injected.[19,20] Generally, if the RSD of CF is the same as or less than 20%, the constructed linear model is considered representative.[20] According to Notice No. 2022-26 from the Korean Ministry of Environment, quality control (QC) target values for R^2 and RSD of CF are set at 0.98 or higher and 25% or less, respectively.

As detailed in Table 5, all R^2 values meet the QC target values, whereas the RSD of CF for geraniol does not satisfy this criterion.There are two possible ways to fix this problem. One method is to employ isotope-labeled geraniol as an internal standard to account for the variation in response due to differences in concentration. Another approach is to exclude geraniol from the indicator ingredients. Indeed, geraniol is also found at other essential oils such as palmarosa oil, geranium oil, rose oil, and

Table 5. Characteristics of calibration curves constructed by chromatographic areas of individual or combnations of indicator ingredient candidates obtained by GC-MS.

No.	Chemicals	Taget ions in order of peak intensities (*m/z*)	Coefficient of determination (R^2) for the range of 10–1000 ppm of citronella oil	RSD of CF (%)[a]
1	Citronellal	41, 69, 95	0.9994	12.6
2	Geraniol	69, 41, 68	0.9980	29.1
3	Citronellol	41, 69, 67	0.9979	23.6
4	Citronellal + Citronellol	-	0.9992	15.0
5	Citronellal + Geraniol + Citronellol	-	0.9987	21.0

[a]RSD of CF: relative standard deviation (RSD) of calibration factor (CF), $CF = (A_x)/(C_x)$, where A_x is area of the compound and C_x is the concentraion of the compound.

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lemongrass oil.[17] Therefore, it is better to exclude geraniol from the indicator ingredients for the citronella oil.

Overall, for identifying Java type citronella oil, it is necessary to check as many of the 14 ISO-listed compounds as possible, depending on citronella oil concentration. To determine the content of citronella oil in a given consumer chemical product, using either citronellal alone or a combination of citronellal and citronellol as indicator ingredients can be effective.

Conclusions

In this study, the comprehensive analysis of citronella oil products was performed by both GC-MS and GC-FID methods. The Java type samples showed a surprisingly consistent composition ratio regardless of origin, given that they are NCSs, while the Ceylon type samples showed high variability in composition ratio. The selection of indicator ingredients for content analysis was based on a comprehensive evaluation of their abundance, consistency in composition, and uniqueness. As a result, citronellal and citronellol have emerged as the most reliable indicators due to their consistent presence and strong quantitative performance. Overall, this study outlines a strategy for selecting indicator ingredients for a NCS. Further evaluation of quantitative performance, including the use of an appropriate internal standard, will be conducted in the near future.

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